

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 07-062218

(43)Date of publication of application : 07.03.1995

(51)Int.Cl.

C08L 71/02
C08K 5/56

(21)Application number : 05-232519

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(22)Date of filing : 25.08.1993

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(54) ROOM TEMPERATURE CURING COMPOSITION

(57)Abstract:

PURPOSE: To obtain the subject composition, containing a specific silicon- containing polymer, a filler and a solid catalyst, excellent in fluidity and elongation and strength of a cured product and useful as sealing materials, adhesives, etc.

CONSTITUTION: This composition contains (A) an organic polymer composed of a polyoxyalkylene, obtained by polymerizing an alkylene oxide such as a 2-4C alkylene oxide with an initiator having ≥ 3 hydroxyl groups in one molecule using a composite metallic cyanide complex such as zinc hexacyanocobaltate as a catalyst and having ≥ 5000 number-average molecular weight and further ≥ 0.3 silicon-containing group expressed by the formula SiXaR_{13-a} [R1 is a 1-20C (substituted) monovalent hydrocarbon group; X is a hydrolyzable group; (a) is 1-3] based on one molecule on the average of the whole molecule, (B) a filler such as silica or carbon black and (C) a curing catalyst such as dibutyltin dilaurate. Furthermore, the component (C) is used in an amount of preferably 0.001-10 pts.wt., especially 0.01-5 pts.wt. based on 100 pts.wt. component (A).

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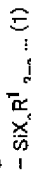
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CLAIMS

[Claim(s)]

[Claim 1] A main chain makes a composite metal cyanide complex (D) a catalyst, and it consists of a with a number average molecular weights of 5000 or more produced by polymerizing alkylene oxide in an initiator (E) which has three hydroxyl groups even if small per monad polyoxyalkylene polymer (F). A room-temperature-curing nature constituent which becomes considering an organic polymer (A), a bulking agent (B), and a curing catalyst (C) which have a silicon content group shown with a following general formula (1) by a total of 0.3 or more molecule averages per monad as the main ingredients.



(R¹ in formula is a univalent hydrocarbon group substitution of the carbon numbers 1-20, or unsubstituted.) X is a hydrolytic basis, a is 1, 2, or 3.

[Claim 2] A room-temperature-curing nature constituent of Claim 1 which is a complex in which a composite metal cyanide complex (D) uses zinc hexa cyanocobaltate as the main ingredients.

[Claim 3] A room-temperature-curing nature constituent of Claim 1 which is at least one sort as which alkylene oxide is chosen from ethylene oxide, propylene oxide, and butylene oxide.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001] [Industrial Application] This invention relates to the room-temperature-curing nature constituent hardened under hygroscopic-surface-moisture existence.

[0002] [Description of the Prior Art] The method of using it for a sealing material, adhesives, etc. using the hardening reaction of various kinds of compounds which have a hydrolytic silicon group at the end which is known as conventional, for example, modified silicone, system resin is known well, and is a useful method industrially.

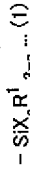
[0003] It is desirable to have viscosity moderate at the time of combination and use, and in order for these to make the rubber elasticity which is rich in the dynamic characteristic of a hardened material, especially pliability reveal further, it is desirable to have a fixed molecular weight.

[0004]

[Problem(s) to be Solved by the Invention] The publicly known polymer which has such an end hydrolytic silicon group is proposed by JP.S45-36319, JP.S46-17553B, etc., for example. It is proposed by JP.S59-230024.A etc. about the thing using the polyether compound of many organic functions especially as a main chain.

[0005] However, the thing depended on these methods of introducing a hydrolytic silicon group after a polyfunctional halogenated compound's tying the polyether compound of low molecular weight, setting it comparatively and carrying out Polymer Division quantification, That a reaction becomes a multi stage story, that a lot of salts carry out a byproduction, that molecular weight distribution (M_w/M_n) spreads considerably and becomes hyperviscosity considerably, and when it was going to make viscosity of a polymer low conversely, since the content of the low molecular weight body increased, there was a fault of the elongation of a hardened material falling. Since bridge construction was easily built by forming many organic functions, it was difficult to obtain the polyether compound of the actually desirable amount of Polymer Division by this method.

[0006] [Means for Solving the Problem] This invention tends to cancel such a fault and a main chain makes a composite metal cyanide complex (D), a catalyst, It consists of a with a number average molecular weights of 5000 or more produced by polymerizing alkylene oxide in an initiator (E) which has three hydroxyl groups even if small per monad polyoxyalkylene polymer (F). It is going to provide a room-temperature-curing nature constituent which becomes considering an organic polymer (A), a bulking agent (B), and a curing catalyst (C) which have a silicon content group shown with a following general formula (1) by a total of 0.3 or more molecule averages per monad as the main ingredients.



(R¹ in formula 1 is a univalent hydrocarbon group substitution of the carbon numbers 1-20, or unsubstituted.) X is a hydrolytic basis, a is 1, 2, or 3.

[0007] A polyoxyalkylene polymer (F) used as a main chain of an organic polymer (A) in this invention, A thing of a hydroxyl group end which makes a composite metal cyanide complex (D) a catalyst, makes alkylene oxide react to initiators, such as a hydroxy compound which has three hydroxyl groups even if small per monad, and manufactures is preferred.

[0008] By using a composite metal cyanide complex (D), M_w/M_n is narrower than a polyoxyalkylene polymer manufactured using the conventional alkaline metal catalyst, it is the amount of Polymer Division more, and it is possible to obtain a polyoxyalkylene polymer (F) of hypoviscosity more. Although a functional group number of a polyoxyalkylene polymer (F) can be arbitrarily controlled with the number of hydroxyl groups of an initiator (E) to a still more desirable thing, when a molecular weight is made equivalent, viscosity becomes low, so that it is many organic functions.

[0009] It is not based on a functional group number of a polyoxyalkylene polymer (F), but the physical properties of a cured body after combination of an organic polymer (A) can be freely controlled by content of a silicon content group. Therefore, physical properties, such as intensity and elongation, are the same, and a constituent using an organic polymer (A) of hypoviscosity can be obtained. Although the number of hydroxyl groups per monad of an initiator (E) used for this invention is three or more, it is preferred that they are 3-6 pieces from balance of physical properties, such as these viscosity, intensity, and elongation.

[0010] A complex which uses zinc hexa cyanocobaltate as the main ingredients as a composite metal cyanide complex (D) is preferred, and the ether and/or an alcoholic complex are preferred. The presentation can use what is intrinsically indicated to JP.S46-27250B. As ether, glyme, a jig lime, etc. are preferred, and glyme is especially preferred from handling at the time of manufacture of a complex. t-butanol indicated to JP.H4-145123.A as alcohol is preferred.

[0011] As a polyoxyalkylene polymer (F), a polyoxyethylene compound, a polyoxypropylene compound, a polyoxy butylene compound, a polyoxy hexylene compound, polyoxy tetramethylen compounds, and/or these copolymers are mentioned. Especially desirable polyoxyalkylene polymers are polyoxypropylene triol and polyoxypropylene tetraol.

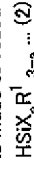
[0012] R¹ in a general formula (1) is a univalent organic group substitution of the carbon numbers 1-20, or unsubstituted, and are a with a carbon number of eight or less alkyl group, a phenyl group, and a fluoro alkyl group preferably. They are a methyl group, an ethyl group, a propyl group, a propenyl group, a butyl group, a hexyl group, a cyclohexyl group, a phenyl group, etc. especially preferably.

[0013] X in a general formula (1) is a hydrolytic basis, for example, there are a halogen atom, an alkoxy group, an acyloxy group, an amide group, an amino group, an aminoxy group, a KETOKISHI mate group, an acid-amide group, a hydride group, etc. As for a carbon number of a hydrolytic basis which has a carbon atom among these, six or less are preferred, and four especially or less are preferred. The desirable hydrolytic basis can illustrate a with a carbon number of four or less lower alkoxy group.

[0014] In a general formula (1) is 1, 2, or 3, and it is preferred that it is especially 2 or 3.

[0015] Next, a manufacturing method of an organic polymer (A) is explained. As for an organic polymer (A) in this invention, what introduces a silicon content group into an end of a polyoxyalkylene polymer (F) which has a functional group so that it may state below, and is manufactured is preferred. Such a compound is liquefied at a room temperature, and when a hardened material holds adaptability and uses for a sealing material, adhesives, etc. also at low temperature comparatively, it is provided with the desirable characteristic.

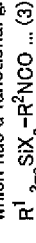
[0016] (**) A method to which a hydrosilyl compound expressed with an end of a polyoxyalkylene compound which has a functional group by what introduced an olefin group, and a general formula (2) is made to react.



(R¹ in formula 2, X, and a are the same as the above.)

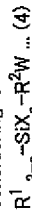
As a method of introducing an olefin group here, A compound which has an unsaturation group and a functional group is made to react to terminal hydroxyl groups of a polyoxyalkylene compound. How to combine by ether bond, ester bond, a urethane bond, carbonate combination, etc., Or when polymerizing alkylene oxide, a method of introducing an olefin group into a side chain, etc. are mentioned by adding and carrying out copolymerization of the olefin group content epoxy compounds, such as allyl glycidyl ether.

[0017] (**) A method to which a compound expressed with an end of a polyoxyalkylene compound which has a functional group by a general formula (3) is made to react.



(R^1 in formula 1, X , and a are the same as the above.) R^2 is a divalent hydrocarbon group of the carbon numbers 1–17.

[0018] (***) A method to which W basis of a silicon compound expressed with a general formula (4) to this isocyanate group is made to react, after making polyisocyanate compounds, such as tolylene diisocyanate, react to an end of a polyoxyalkylene compound which has a functional group and considering it as an isocyanate group end.



(R¹ in formula 1, R², X, and a are the same as the above.) Active hydrogen containing group as which W was chosen from a hydroxyl group, a carboxyl group, a sulfinydril group, and an amino group (the 1st class or the 2nd class).

[0019](**): A method which introduces an olefin group into an end of a polyoxyalkylene compound which has a functional group and to which the olefin group and a sulphydryl group of a silicone compound expressed with a general formula (4) whose W is a sulphydryl group are made to react. [0020] silicon content cardinal number is 0.3 or more per monad in a total molecule average.

[0020] A silicon content cardinal number is 0.3 or more per monad in a total molecule average.

[0021] As an organic polymer (A) in this invention, an organic polymer of the number average molecular weights 5000–30000 can be used. If elongation will become low and a number average molecular weight exceeds 30000 firmly [a hardened material] when a number average molecular weight of an organic polymer (A) is lower than 5000, pliability and elongation of a hardened material are satisfactory, but viscosity of the polymer itself [this] becomes remarkably high, and practicality becomes low. As for especially a number average molecular weight, 8000–30000 are preferred. In order to control the physical properties of a cured body depending on a use, it can also be used with a mixture with same organic polymer using an initiator which has three or less hydroxyl groups.

[2022]In order to stiffen an organic polymer in this invention, a curing catalyst (B) is indispensable. When not using a curing catalyst (B), the crosslinking reaction of a hydrolytic silicon group cannot obtain significant reaction velocity.

obtaining significant reaction velocity. [0023]As a curing catalyst (B), a publicly known compound can be used as a catalyst of hydrolysis of a hydrolytic silicon group, and a condensation reaction. Namely, amine salt, 2-ethylacrylate, and a basic catalyst can be used at the time, such as metal salt, dibutyl amine, 2-ethylhexoate of carboxylic acid, at the time, such as an alkyl titanate, an organic silicon titanate, tin octylate, and dibutyltin dilaurate. Although it is good to use it in the range of 0.001 – 10 weight section to organic polymer (A) 100 weight section as amount of curing catalyst used, it is preferred to carry out 0.01–5 weight-section use especially.

[0024]As a bulking agent (C) in this invention, can use a publicly known bulking agent, and specifically, Fumes silica, sedimentation nature silica, a silicic acid anhydride, hydrous silicic acids, and a bulking agent like carbon black. Calcium carbonate, magnesium carbonate, diatomite, calcination clay, clay, Fibrous fillers, such as bulking agents, such as talc, titanium oxide, bentonite, organic bentonite, ferric oxide, a zinc oxide, an active white, hydrogenation castor oil, and a melt balloon, asbestos, glass fiber, and a filament can be used.

[0025] In this invention, a plasticizer can be used arbitrarily. As a plasticizer, can use a publicly known plasticizer and specifically Dioctyl phthalate, Phthalic ester, such as dibutyl phthalate and butylbenzyl phthalate, Dioctyl adipate, Glycol ester, such as aliphatic-carboxylic-acid ester, pentaerythritol ester, such as succinic acid isodecyl, dibutyl sebacate, and butyl oleate; Trioctyl phosphate, Phosphoric ester, such as tricresyl phosphate; epoxy plasticizer; chlorinated paraffins, such as epoxidized soybean oil and epoxy stearic acid benzyl, etc. can be independent, or can use it with two or more sorts of mixtures.

[0026] The constituent of this invention can contain still more publicly known various additive agents etc. As an additive agent, adhesion grant agents, such as phenol resin and an epoxy resin, paints, varnishes, etc. can be used. As an ultraviolet ray absorber, various kinds of antiaging agents, an ultraviolet ray absorber, etc. can be used.

[0027] At a room temperature, a room-temperature-curing nature resin composition of this invention is hardened under hygroscopic-surface-moisture existence, and can be especially used as an object for elastic sealant, and an object for adhesives.

[0028]

[Example]Although working example explains this invention concretely below, this invention is not limited only to these working example. The example of manufacture of the organic polymer which

uses the example of manufacture of an organic polymer (A) for the next by the reference examples 1-2, and is used for a comparative example by the reference examples 3-4 is shown first.

[0029] [Reference example 1] By a method given in JP,H3-72527,A, propylene oxide is polymerized with a zinc hexa cyanocobaltate glyme complex by using the glycerin propylene oxide addition of the molecular weight 1000 as an initiator, Polyoxypolyene triol of the number average molecular weight 20000 was obtained, terminal hydroxyl groups is changed into allyl ether groups, the addition reaction of the methyl dimethoxysilane was further carried out by having made chloroplatinic acid into the catalyst, and the organic polymer (P1) which has an average of 1.3 hydrolytic silicon groups per molecule was obtained.

[0030] Reference example 2) By a method given in JP-H3-72527-A, propylene oxide is polymerized with a zinc hexa cyanocobaltate glyme complex by using pentaerythritol as an initiator. Polyoxypolypropylene tetraol of the number average molecular weight 20000 was obtained. terminal hydroxyl groups is changed into allyl ether groups, the addition reaction of the methyl dimethoxysilane was further carried out by having made chloroplatinic acid into the catalyst, and the organic polymer (P2) which has an average of 1.1 hydrolytic silicon groups per monad was obtained.

(P-2) which has an average of 1.1 hydrolytic silicon groups per molecule was obtained. [0031] Reference example 3: By a method given in JP-H3-75271A, propylene oxide is polymerized with a zinc hexa cyanocobaltate glyme complex by using the diethylene glycol propylene oxide addition of the molecular weight 1000 as an initiator. Polyoxypylene diol of the number average molecular weight 20000 was obtained, terminal hydroxyl groups is changed into allyl ether groups, the addition reaction of the methyl dimethoxysilane was further carried out by having made chloroplatinic acid into the catalyst, and the organic polymer (P-3) which has an average of 1.4 hydrolytic silicon groups per molecule was obtained.

groups per molecule was obtained. [0032]Reference example 4) Polyoxypropylene diol of the number average molecular weight 3000 is made to react to tris(chloromethoxy) benzene by the method of a description at JP.S60-12363B. After making terminal hydroxyl groups react to allylchloride furthermore and considering it as end allyl ether groups, the addition reaction of the methyl dimethoxysilane was further carried out by having made chloroplatinic acid into the catalyst, and the organic polymer (P4) was obtained. The number average molecular weight of this organic polymer was 8000.

average molecular weight of this organic polyimide was 6000. [0033] Working example 1 and 2 and comparative example 1 As opposed to organic polymer (P1-P3) 100 weight section compounded by the reference examples 1-3, Calcium carbonate 160 weight section, titanium oxide 20 weight section, dioctyl phthalate 60 weight section, After adding and kneading hydrogenation castor oil 5 weight section, phenolic antioxidant 1 weight section, and 3-(2-aminoethyl) aminopropyl methyl dimethoxysilane 1 weight section, Dibutyltin dilaurate 1 weight section was added, and it kneaded further, and extended to the 2-mm-thick sheet shaped, and it set for seven days to 50 °* and the constant temperature/humidity chamber of 80% of humidity, and it was recuperated to them. The hardened material was pierced with the JIS No. 3 dumbbell, and performed physical-properties measurement. It is ductility (%) at the time of intensity (kg/cm²) and a fracture at the time of a 50% modulus (M₅₀) (kg/cm²), and a fracture. Organic polymer viscosity based on 25 °* and BH type viscosity meter (cps) is summarized in Table 1.

(based
[0034]

[Table 17]

No.	实施例 1	实施例 2	比较例 1
有機重合体	P 1	P 2	P 3
M ₆₀	1. 2	1. 1	1. 1
破断時強度	5. 2	4. 9	5. 4
破断時伸度	720	680	750
有機重合体粘度	11000	8500	18000

[0035][Comparative example 2] The viscosity of the organic polymer (P4) compounded by the reference example 4 was 20000 cps (a measuring condition is the same as the above).

[0036]

[Effect of the Invention]. Use the composite metal cyanide complex catalyst of this invention, and have intrinsically the polyoxyalkylene polymer produced by polymerizing alkylene oxide in the initiator which has three or more hydroxyl groups in a main chain. The room-temperature-curing nature constituent which uses a hydrolytic silicon group content organicity polymer as a hardening component has the effect of having the outstanding elongation and strength properties, and low viscosity as compared with the polymer which carries out chain extension of the polymer of comparatively a low number average molecular weight known conventionally, and manufactures it.

[Translation done.]